Wood Sci Technol (2009) 43:69–83
DOI 10.1007/s00226-008-0208-3

ORIGINAL

Influence of heat treatment on antioxidant properties and colour stability of beech and spruce wood and their extractives

A. Ahajji · P. N. Diouf · F. Aloui · I. Elbakali · D. Perrin · A. Merlin · B. George

Received: 9 October 2007 / Published online: 23 July 2008
© Springer-Verlag 2008

Abstract Heat treatment of wood in absence of oxygen and under mild conditions allows for obtaining a material with many interesting properties, such as enhanced dimensional stability and increased biological durability. The aim of this work was to study the influence of a thermal treatment on the antioxidant activity of the extractives of two wood species – beech and spruce – by using the DPPH method and quantifying the formation of phenoxyl radicals using ESR as wood and extractives are exposed to light irradiation. The relationship between the kinetics of formation of free radicals in the extracts of heat-treated wood and the antioxidant properties is discussed. Links with colour modification are discussed.

Introduction

Heat treatment of wood at a moderate temperature (200–250°C) under inert atmosphere (to avoid oxidative degradation) leads to a material referred to as torrefied wood or heat-treated wood. The environmental requirements which become more and more severe should favour the applications of such treated woods insofar as durability or dimensional stability of the material can be enhanced without using some polluting treatments (CCA, etc.). The French process is referred

---

A. Ahajji · F. Aloui · I. Elbakali · D. Perrin · A. Merlin · B. George (✉)
LERMAB – UMR INRA/ENGREF/UHP 1093, Nancy-Université, Université Henri Poincaré,
B.P. 239, 54506 Vandoeuvre-les-Nancy Cedex, France
e-mail: Beatrice.George@lermab.uhp-nancy.fr

P. N. Diouf
Département des Sciences du Bois et de la Forêt, Faculté de Foresterie et de Géomatique,
Université Laval, Quebec, QC, Canada G1K 7P4

I. Elbakali
Département de Chimie Physique, Faculté des Sciences Dhar Mahraz,
Université Sidi Mohamed Ben Abdellah, BP 1796 Fès, Fes, Morocco

to as retification (a contraction of the words “reticulation” and “torrefaction”) and was first developed at Ecole des Mines de Saint-Etienne (Bourgois and Guyonnet 1988). A few companies now operate under a license possessed by NOW S.A. company. Wood is dried to about 12% moisture prior to the treatment which consists of slowly heating up to a temperature between 210 and 240°C in a nitrogen atmosphere with less than 2% oxygen (Van Acker et al. 2004). In this temperature range, the hemicelluloses are the most affected macromolecules of wood: from 180°C, depolymerization of these components is accompanied by the release of low molecular weight compounds such as acetic acid, furfural, methanol, CO_2 (Avat 1993).

The released acetic acid further contributes to the degradation of hemicelluloses and amorphous cellulose. The degradation of amorphous cellulose is evidenced by the increase of crystallinity of cellulose which is observed by RMN spectroscopy on wood heated at this temperature range (Sivonen et al. 2002).

Such a spectroscopic technique also highlights a weak increase in reticulation of lignins (Hawkes et al. 1993; Sivonen et al. 2002). In the temperature range of concern, the limited degradation of lignins causes the formation of reactive sites where intermediates resulting from the hemicelluloses degradation can condense (Sandermann and Augustin 1964).

The thermal degradation of extracts is also responsible for the release of by-products like polycyclic aromatic hydrocarbons (phenanthrene, acenaphtylene) which give torrefied wood its characteristic and persistent odour (Tjierdsma et al. 1998; Kamdem et al. 2000). These chemical modifications confer properties to the heat-treated wood which are missing or insufficient in native wood (Mouras et al. 2002; Kamdem et al. 2002) such as reduction of anisotropy and hygroscopy, improvement of dimensional stability, resistance to the biological – particularly fungal – attacks.

Work by Ishiguri et al. (2003) on thermal treatment of sugi demonstrates the important role of extracts in colour evolution of wood under irradiation. They exposed extracts of smoke-heated sugi to UV irradiation and showed that the *n*-hexane soluble fraction contains the substances responsible for yellowing of heartwood and the acetone soluble fraction contains those responsible for reddening.

Varga and Van der Zee (2008) steamed some woods and concluded that dissolving, oxidizing, and decomposing of extractives are the main cause for the colour change. Wood which contains a large quantity of water soluble extractives (e.g. black locust and merbau) present the most intensive colour changes after steam treatment.

A recent study (Ahajji et al. 2003) focused on colour modification of torrefied wood of three species – beech, spruce and eucalyptus – and showed that torrefaction strongly affects wood colour with a large decrease of lightness for the three species. Colour is all the more modified as torrefaction temperature is increased; but above roughly 220°C darkening does no longer depend on the treatment temperature.

In the present work, the aim was to study the antioxidant properties of torrefied wood and its extracts. Antioxidant polyphenolic extracts are thought to be involved in resistance to fungi and also in colour stability. As these properties are modified by torrefaction, the quality of extracts – phenol content and antioxidant capacity – should be modified as well.

Materials and methods

Reagents

Methanol used was of HPLC grade (99.9%) from MERCK. 2,2-Diphenyl-1-picrylhydrazyl DPPH (>85%) and Folin-Ciocalteu reagent (ref. 47741) were purchased from FLUKA. Sodium carbonate (99%) and gallic acid (98%) were provided by PROLABO and ACROS, respectively.

Test specimens and heat treatment

Heat-treated samples from two wood species – beech (*Fagus sylvatica L.*) and spruce (*Picea abies*) – were kindly provided by Patrick ROUSSET from “Laboratoire Biomasse Energie Environnement” CIRAD, Montpellier. Fifty millimetre thick heartwood planks were treated with an average moisture content of 13% at 210, 235 and 250°C for 1 h (Rousset 2004). For each species, an untreated plank was used as reference. In each plank, samples were cut for testing (dimensions 30 mm × 30 mm × 10 mm, orientations Longitudinal × Tangential × Radial).

Wood extraction

Extraction was carried out with the accelerated extracting system ASE 200® of Dionex Company. After leaching with petroleum ether for 24 h, meal of each wood sample was extracted with a solution of ethanol-water (70/30 v/v) at 100°C under 100 bar pressure in two cycles. The static time of each cycle was 5 min. Extracts were dried in a rotating evaporator under reduced pressure at 40°C; for each extraction, the yield was determined.

Estimation of total phenols

Total phenols were estimated by colorimetric measurements using the Folin-Ciocalteu method according to Singleton and Rossi’s protocol (1965). Methanolic solutions of extracts at 0.1 and 0.2 g/L for beech and spruce, respectively, were prepared to obtain a final absorbance (measured in a Perkin-Elmer Lambda 2 UV-visible spectrophotometer) below 0.5. A 2.5-mL aliquot of Folin-Ciocalteu reagent (diluted ten times by distilled water) was added to 0.5 mL of the methanolic solution of extracts. After 8 min, 2 mL of an aqueous sodium carbonate solution (75 g/L) was added to the mixture. The assay tubes were kept for 5 min in a water bath at 50°C and then cooled in a water-ice bath for 10 min. Results are expressed in gallic acid equivalents per amount of extract. Calibration is achieved with gallic acid methanolic solutions (10-80 μg/mL).

ESR analysis

ESR spectra were plotted using a Brucker ER 200 D spectrometer (X-band) equipped with a TE102 cavity. Samples can be submitted to ultraviolet–visible irradiation by a xenon vapour lamp (OSRAM XBO 1000W). The light flux delivered is 30 mW/cm^2 at 366 nm, i.e. 300 times the average solar flow on the surface of the ground at this same wavelength. ESR measurements were made with a four Gpp field modulation. Not any fine structure of the ESR signals could be detected even by decreasing the field modulation. Wood samples and wood extracts were respectively conditioned in the form of sticks (3 mm × 3 mm × 35 mm) and powder. All experiments were carried out in quartz tubes, transparent to the totality of the spectrum emitted by the xenon vapour lamp in the UV–visible range, at room temperature and atmosphere. Detection was made in such a way that the signal obtained corresponds to the first derivative of the curve of absorption. The position of ESR signals is expressed by the Landé factor, g, which was determined by comparison with the spectrum of free radical DDPH in solid state ($g = 2.0023$).

DPPH radical assay

The radical scavenging capacities for each extract were estimated by the DPPH method (see e.g. Brand-Williams et al. 1995). Equal volumes of a methanolic solution of extract and a 200-μM methanolic solution of DPPH were mixed in a stopped-flow apparatus (SFA-11 rapid kinetic accessory, HIGH-TECH Scientific, Salisbury, England) coupled with a UV–visible spectrophotometer (Lambda 2, Perkin-Elmer). The decrease of absorbance at 30°C was measured at 516 nm. For each solution of extract tested, the reaction kinetics was plotted (Fig. 1).

From these graphs, the percentage of DPPH reacting after 30 min was determined. All experiments were performed in triplicate. Radical scavenging activity of each extract was defined as the effective concentration EC$_{50}$ at which

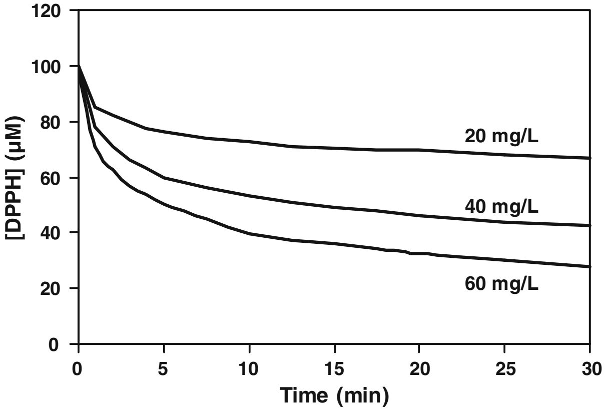

Fig. 1 Reaction between DPPH (100 μM) and untreated beech wood extracts at different concentrations. DPPH concentration as a function of time

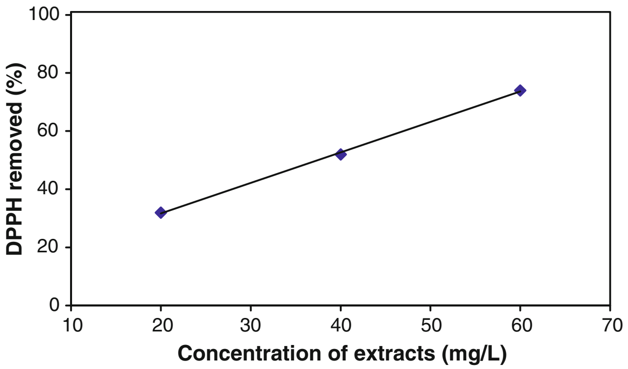

Fig. 2 Reaction between DPPH (100 μM) and untreated beech wood extracts at different concentrations. Determination of EC_{50} by interpolation

50% of DPPH was reacted in the present conditions. EC_{50} is determined by interpolation of the percentage of DPPH reacting as a function of the initial extract concentration (Fig. 2).

Colour measurement and ageing system

Colour was measured in the CIE L*a*b* system using a spectrocolorimeter Spectrocolor (Dr Lange GmbH) with a standard illuminant D65 and 10° circular illumination. In this colour space, a colour is defined by its Cartesian chromatic coordinates: lightness L* which varies from 0 (black) to 100 (white), and a* and b* coordinates which define the chromaticity plane; the colours vary from green to magenta along the a* axis and from blue to yellow along the b* one. This system has often been used to measure the natural colour of woods (Janin 1987; Mazet 1988) or to trace colour modifications during photochemical ageing of abies (Dirckx et al. 1992) or oak (Mazet et al. 1993). Nevertheless the CIE L*a*b* space is not uniform and it produces a weak correlation with visual perceptions (Chrisment 2000). Therefore, to measure colour evolution during a transformation, it is more pertinent to use the CIE L*C*h* system which is more homogeneous and simply derives from the CIE L*a*b* system by changing cartesian coordinates to cylindrical ones in the chromaticity plane [a*, b*]: chroma is defined by $C^* = (a^{*2} + b^{*2})^{1/2}$ and hue angle by $h^* = \arctan\ (b^*/a^*)$. Mean values of chromatic coordinates were calculated from ten measurements at different positions on the sample. The measuring area was 0.8 cm^2. Colour variations induced by thermal treatment or by irradiation are expressed as the overall colour difference ΔE^* given in the CIE L*a*b* system by:

$$\Delta E^* = [\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}]^{1/2}$$

Accelerated ageing of raw and heat-treated woods was done in a SEPAP chamber (MPC, France) equipped with middle pressure mercury vapour lamps with a light flow of 5 mW cm^{-2} at 365 nm. Samples, rotating at constant speed and distance from the sources, were exposed for 300 h at 50°C. It was checked that, without irradiation, wood colour is stable at this temperature for at least 300 h.

Results and discussion

Wood extracts

Table 1 shows yields, phenol contents and antioxidant capacities of wood extracts from beech and spruce.

Heat treatment clearly increases the extract yield for beech whereas yields are almost unchanged for treated and untreated spruce wood as Ishiguri et al. (2000) observed in black heartwood of smoke-heated sugi. Hakkou et al. (2003) studied the variation of extract yield during heat treatment of beech and found that it was more important at 160°C probably due to hemicelluloses decomposition. Nevertheless, compositions of both woods are quite similar [spruce wood composition consists in 40.4% cellulose, 31.1% hemicelluloses and 28.2% lignin (Fengel et al. 1978) and beech wood in 44.5% cellulose, 30.2% hemicelluloses and 22.2% lignin (Fengel et al. 1979)] and it is difficult to interpret our results only on the basis of hemicelluloses contents. Nevertheless, different structures of hemicelluloses in hard- and softwoods could explain our observations. Hardwoods mainly contain xylan in the 14–30% range and only 1–4% of glucomannan whereas these percentages are nearly reversed in the case of softwoods (5–11% for xylan and 14–20% for glucomannan). Further studies on the stability of hardwoods and softwoods hemicelluloses are necessary.

Heat treatments at temperatures higher than 200°C deeply modify the chemical composition of wood although its macroscopic and microscopic organizations do not seem to be much affected for temperatures not exceeding 300°C (Avat 1993). According to Avat (1989), the extractable components of wood behave as catalysts, at least at the beginning of the heat treatment. Then, at higher temperatures, they inhibit the reactions of thermal degradation (Roy et al. 1990). The amount of extractable matter varies during heat treatment: some compounds are volatilized whereas others appear due to a more important wood degradation (Kilcullen 1995). During pyrolysis lignin and carbohydrates (polysaccharides) are gradually converted into volatiles and “extractive-like material”, which in turn is partly degraded together with the original extractives, into various volatile products. In addition,

Table 1 Extraction yields, phenol contents and antioxidant capacities of wood extracts of both species, before and after heat treatment

		Untreated	210°C	235°C	250°C
Yield (%)	Beech	4.5	10.0	11.0	9.9
	Spruce	5.2	5.9	5.7	5.0
Phenol content (%)	Beech	20	28	37	42
	Spruce	19	20	22	25
EC_{50} (mg L^{-1})	Beech	37	35	21	19
	Spruce	79	69	53	42

heating carbohydrates probably leads to some extent to the formation of unsaturated nonvolatile material, i.e., UV-detectable "lignin-like material" (Kotilainen 2000).

The influence of the native extracts of a species and of the extracts formed during the treatment on the characteristics of modified heated-wood is still badly known.

Total phenol contents

Total phenols were quantified for extracts of untreated and heat-treated beech and spruce wood. The phenol content of extracts significantly increases after the treatment (Table 1). One can notice that the higher the treatment temperature, the more important the total phenol content. This may be explained by the degradation of lignin and of nearly extractable compounds during heat treatment (Avat 1993). It is noteworthy that the glass transition temperature of lignin (between 160 and 190°C) is largely exceeded by our heat treatment temperatures (210, 235 and 250°C). Under our conditions, phenomena of lignin condensation are accompanied by a partial decomposition of lignin macromolecules probably due to cleavages of *β-O*-aryl ether interunit linkages (Nuopponen et al. 2005) to low-molecular-weight products resulting in the increase of total phenol contents and concentration of free phenoxyl radicals. The increase of the total phenol content is larger in the case of beech wood compared to spruce wood. This observed difference mainly originates from intrinsic properties of lignin which differ for hardwoods and softwoods: softwood lignin consists almost exclusively of guaiacyl type lignin derived from coniferyl alcohol whereas hardwood lignin is mainly constituted of syringyl units, derived from sinapyl alcohol that has two methoxyl groups, which results in lignin with a larger number of ether bonds.

Beech extracts in solution (Fig. 3) exhibit UV absorbance at 280 nm (typical of phenolic compounds) in good agreement with the phenol contents in Table 1. A shoulder near 320 nm appears after heat treatment. An increase of absorbance above

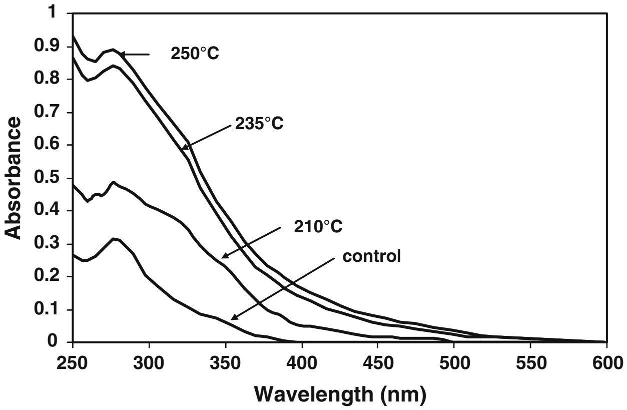

Fig. 3 UV-visible spectra of extracts (0.04 g/L in MeOH) from beech wood before and after heat treatment

400 nm agrees with the increasing browning of extracts by heat treatment. Similar spectra were obtained for spruce extracts.

Free radical scavenging ability of extracts

The antioxidant activity of the extracts of both wood species, untreated and heat treated, was studied by examining the concentration of extracts necessary to decrease DPPH concentration by 50% – the efficient concentration EC_{50} – as described above. The lower the value of EC_{50}, the more effective the extract. All samples, untreated and heat treated, exhibit antioxidant activities (Table 1). For each species, antioxidant activity increases with the heat treatment temperature. We can also observe that extracts from beech wood are more effective from the antioxidant point of view than extracts from spruce wood. As expected, antioxidant activity increases with the phenol content of the extracts, but phenols produced by heat treatment seem to be more antioxidant in spruce than in beech wood. It would be useful to study the modification of antioxidant capacities of native extracts of both species by heat treatment.

ESR analysis

Antioxidant capacity of the extract of heat-treated wood was also quantified by determining the rate of formation of the phenoxyl radical (in our case, radicals are formed by irradiation of the extracts in the solid state) by ESR. Such a parameter measures the ability and the ease of the extract to form phenoxyl-free radicals. It is clear that the faster the reaction, the more important the antioxidant capacity.

First, the ESR signals of raw and torrefied samples were examined, then the signals of the extracts thereof. The characteristics of the ESR singlet recorded are reported in Table 2. Note that an arbitrary value of 1 was allotted to the height of the signal recorded for each control sample, i.e. untreated sample or its extracts. Then, the relative intensity α was calculated as a ratio of the ESR signal of the heat-treated sample to the ESR signal of the corresponding control.

Table 2 Parameters of ESR spectra of beech and spruce wood solid samples and beech and spruce wood extracts, before and after heat treatment

		Width (gauss)		*g*		Relative intensity α	
		Wood	Extracts	Wood	Extracts	Wood	Extracts
Beech	Control	9.1	6.8	2.0046	2.0032	1	1
	210°C	7.7	6.6	2.0046	2.0034	8.4	1.7
	235°C	7	6.6	2.0046	2.0030	23.1	5.0
	250°C	6.7	5.6	2.0046	2.0032	26.8	7.3
Spruce	Control	7.3	7.0	2.0045	2.0033	1	1
	210°C	9.0	7.0	2.0045	2.0026	5.5	1.5
	235°C	8.3	6.7	2.0045	2.0024	7.4	2.4
	250°C	8.0	6.0	2.0045	2.0030	8.1	1.9

Whatever the species and the treatment of wood, the same singlet signal was observed for all the samples, identical in terms of shape and position, which is characteristic of phenoxyl radicals (Merlin and Deglise 2001). Nevertheless, the width is more reproducible for extract powder than for solid woods because each wood sample is unique. The values of *g* are slightly different for woods and extracts: extracts contain simple phenols whereas free radicals in woods are partly formed on lignins. It was observed that heat treatment strongly increases the free radical production in wood but to a less extent in extracts. For each species, ESR signal intensities of heat-treated wood samples and their resulting extracts are greater than those of untreated ones. It can also be pointed out that they clearly increase with the treatment temperature.

ESR analyses of beech wood and extracts were then performed while irradiating samples for 1 h. In order to compare kinetics of formation of phenoxyl radicals during irradiation, the relative variations $(I_t - I_0)/I_0$ were followed up and are shown in Fig. 4 for beech wood and in Fig. 5 for its extracts.

Values of ESR signals at the beginning (I_0) and after 1 h (I_∞) of irradiation are reported in Table 3; 1 h may be considered nearly infinite time. Relative I_∞ values correspond to the ratio of the ESR signal for the heat-treated sample to the corresponding control, both recorded after 1 h of irradiation i.e. $I_\infty/I_{\infty\ \mathrm{control}}$.

A high and clear increase of phenoxyl radicals formed under the effect of irradiation of untreated wood and its corresponding extracts was observed. This increase is much less important for heat-treated samples. The stabilization of the ESR signal for wood samples is reached after 50 min of irradiation compared to a few minutes (roughly 5 min) in the case of the extracts. The kinetics of reaction is always faster for the extracts than for wood. The rates of radical formation from wood and from extracts appear to be more important before treatment and decrease

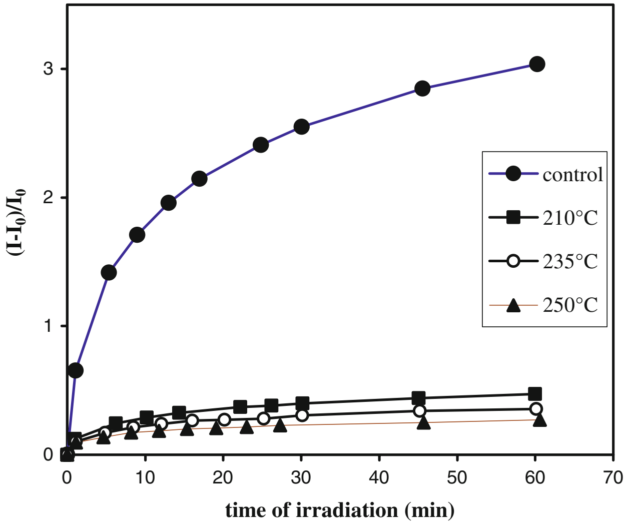

Fig. 4 Relative intensity of ESR signal of beech wood during irradiation as a function of time

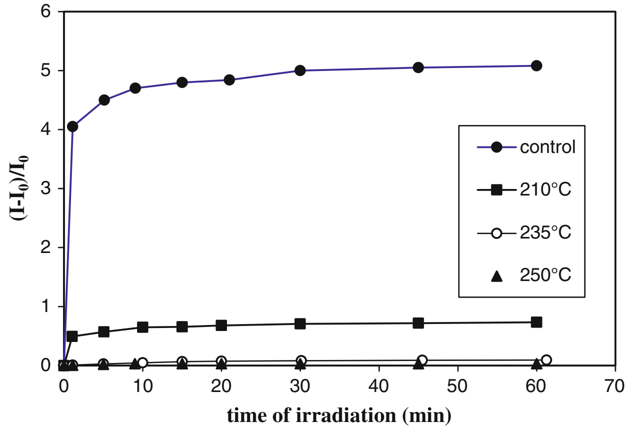

Fig. 5 Relative intensity of ESR signal of beech wood extracts during irradiation as a function of time

Table 3 Intensity of ESR signals of beech wood and extracts before (I_0) and after (I_∞) irradiation (values normalized to the control untreated samples wood or extract)

	$(I_\infty - I_0)/I_0$		Relative intensity I_∞	
	Wood	Extract	Wood	Extract
Control	3	5.08	1	1
210°C	0.47	0.73	3.1	0.5
235°C	0.36	0.09	7.8	0.9
250°C	0.27	0.03	8.5	1.3

as the heat treatment temperature increases. However, it has to be noticed that the stationary concentrations at the end of irradiation, relative I_∞, are more important for the torrefied wood samples as the treatment temperature is higher.

Studies of wood photodegradation evidenced a relationship between colour modifications and intensity of the ESR signal attributed to phenoxyl-free radicals. Photoproducts responsible for colour alteration have been shown to solely originate from phenoxyl-free radicals through oxidative processes. Phenoxyl radicals absorb visible light and then participate to coloration of wood (Merlin and Deglise 2001). Thus, a treatment which stabilizes wood colour concomitantly induces a reduced concentration of phenoxyl-free radicals (Triboulot 1993).

Colour variations

According to these results regarding wood photodegradation, it seems useful to study the influence of thermal treatment on the colour of samples, in order to bring out relationships with radical species content of wood. For both studied species, heat treatment strongly modifies colour with overall colour differences ΔE* between raw and treated samples bigger than 30 (Table 4). These values are very high; by comparison, overall colour differences for natural wood, measured after 800 h of exposure in our SEPAP chamber, are about twenty for the most light-sensitive woods.

Table 4 Colour alterations induced by heat treatment

		L*	a*	b*	C*	h	ΔE*	α
Beech	Control	76.2	6.9	19.7	20.9	70.8		
	210°C	38.1	7.3	11.5	13.6	57.8	38.9	8.4
	235°C	31.9	3.8	5.4	6.6	54.7	49.6	23.0
	250°C	30.9	3.7	4.5	5.8	51.1	47.9	26.7
Spruce	Control	85.1	2.1	20.1	20.2	84.0		
	210°C	57.3	11.2	17.2	29.4	67.7	29.4	5.5
	235°C	45.6	10.1	20.7	22.0	63.9	40.3	7.4
	250°C	42.2	9.3	16.9	19.2	61.1	43.6	8.1

α is the ratio of the ESR signal intensity of the treated wood sample to the signal of the raw material

For all samples, heat treatment induces a strong decrease of luminance (darkening). These variations are all the more pronounced at higher treatment temperatures. For both species, thermal treatment induces a simultaneous variation of chroma C* and hue angle h*, which evidences a chemical modification of chromophores responsible for the colour of the samples. Some disparities of colour modification can be observed depending on the wood species. For beech, b* coordinate (yellow component) decreases as treatment temperature increases, while a* coordinate (red component) significantly decreases only for the highest temperatures tested, i.e. 235 and 250°C. For spruce, b* is little affected by heat treatment, while a* strongly increases when heat treatment is applied even if it does not vary significantly with the treatment temperature. Results obtained for eucalyptus (Ahajji et al. 2003) were similar to those obtained for beech. Thus, the decrease in hue angle value after heat treatment essentially results from a decreasing b* for hardwood (beech) and from an increasing a* for softwood (spruce).

A positive correlation (Fig. 6) between the intensity of the ESR signal α and the colour change was observed due to the heat treatment, especially for spruce ($R^2 = 0.999$) and to a less extent for beech ($R^2 = 0.888$). Because of the heterogeneity of the material investigated and the limited number of treatment temperature tested, the coefficients obtained appear quite satisfying.

As the formation of radical species is different depending on whether raw or heat-treated samples of both wood species are exposed to a solar-type irradiation, it was found to be useful to compare colour modifications during an accelerated ageing. The aim was to check that the relationship between light stability and phenoxyl radical concentration is still obeyed for heat-treated wood samples. In Table 5, values of the chromatic coordinates obtained after a 300 h accelerated ageing are reported (ΔE^*_{300} was calculated using the initial values L*, a*, b* (before ageing) reported in Table 4). As an example, results obtained during ageing of spruce are plotted in Fig. 7 (similar results were obtained for beech).

For all the samples, overall colour differences ΔE*, with colour of the reference sample before irradiation (of course this reference is unique to each sample) show similar evolutions: ΔE* increases, then stabilizes near 300 h under our experimental conditions.

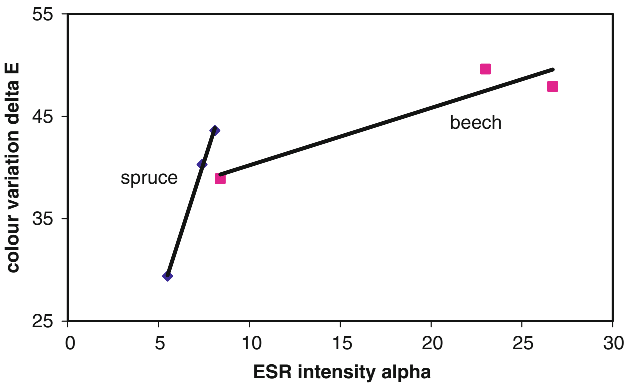

Fig. 6 Correlation between the colour variation and the intensity of ESR signal of heat-treated woods

Measuring stationary colour differences ΔE^*_{300} shows that the colour of heat-treated spruce is more light-resistant than its natural one on the contrary to the case of beechwood (Table 5).

Mitsui and Tsuchikawa (2005) studied light-induced colour changes of wood as a function of temperature and observed that there are no colour changes at −20°C and that changes increase with temperature. It was checked that, without irradiation, the wood colour is stable at 50°C. This does not disagree with observations made under irradiation. Light certainly causes bond-cleavages that lead to formation of free radicals but, at lower temperatures, reduced mobility precludes subsequent chemical transformations.

An ongoing study of other wood species in our laboratory confirms that the colour of heat-treated hardwood is generally less light resistant than the one of softwood. Comparing the values in Tables 4 and 5 enables to find some general trends. First, for both wood species studied, ageing induces decreasing luminance (darkening) of the untreated sample and an increasing luminance (brightening) of the torrefied samples. Thus, heat treatment confers wood a dark colour which brightens when exposed to solar light. Nevertheless, luminance of heat-treated wood remains smaller than that of untreated wood, even after irradiation. Secondly, evolutions of chromatic coordinates a* and b* of heat-treated samples depend on the

Table 5 Influence of the treatment temperature on chromatic coordinates after 300 h of ageing

		L^*_{300}	a^*_{300}	b^*_{300}	ΔE^*_{300}
Beech	Control	67.2	8.9	29.1	13.2
	210°C	53.0	6.8	19.0	16.8
	235°C	40.5	5.3	12.4	11.3
	250°C	41.3	5.1	11.2	13.7
Spruce	Control	72.7	8.5	35.5	20.8
	210°C	66.3	8.3	32.4	10.8
	235°C	56.5	8.3	26.1	10.9
	250°C	45.8	8.2	26.9	15.1

ΔE*300 was calculated using the initial values L*, a*, b* (before ageing) reported in Table 4

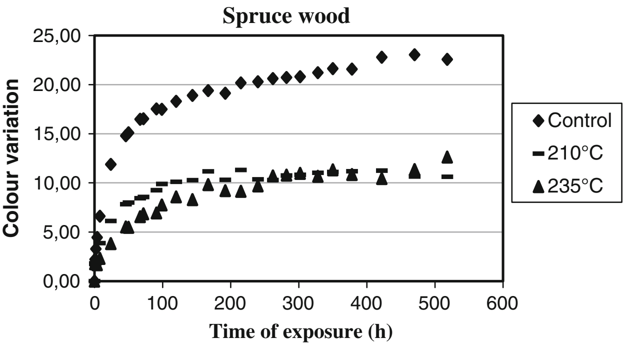

Fig. 7 Modification of the colour, ΔE*, during the photochemical ageing of spruce wood

wood species considered. For spruce, a* coordinate reaches a value $a^*_{300} = 8.2$–8.5 whatever the sample but in the case of treated wood, a* decreases and rapidly stabilizes after 20 h under our experimental conditions, whereas it increases slowly for raw material. For treated and untreated spruce, b* increases during irradiation. This increase is large for the control sample and rather smaller as heat treatment temperature increases. For beech wood, the same slight increase of a* is roughly observed for samples treated at 235 and 250°C. For untreated wood and samples treated at 210°C, evolutions of a* are opposite at the beginning of irradiation. In all cases, b* increases under irradiation.

Monitoring the hue angle h* allows to take into account simultaneous variations of a* and b* during irradiation. For untreated spruce, the continuous decrease of h* during irradiation results from a simultaneous increase of a* and b*, whereas the increase of h* observed for treated wood at the beginning of irradiation is due to a decrease of a* and an increase of b*. For a long ageing time, hue angles of treated and untreated samples stabilize at similar values. For a long-ageing time, hue angles of treated and untreated samples stabilize at similar values. For hardwoods, h* is rather stable for untreated samples because both a* and b* coordinates increase to the same extent, whereas it rapidly increases at the beginning of irradiation for the heat-treated samples due to a slight variation of a* and a quite large increase of b*.

Finally, evolutions of chromatic coordinates of samples treated at 235°C and 250°C are very similar. It seems that there is a temperature beyond which colour stability is no longer affected: at this temperature, a stationary quantity of chromophores responsible for the colour of treated wood seems to be achieved. Similarly, the ESR signal of a non irradiated heat-treated sample strongly increases from 210 to 235°C whereas values measured for 235 and 250°C are very close.

Conclusion

It was shown that the heat treatment of wood increases phenol contents, concentrations of stable phenoxyl-free radicals and antioxidant activities. The increase in the total phenol contents and the phenoxyl radicals can only be accounted to lignin and /or wood extracts because of the hydrogen donor ability of their phenolic functions. By their antioxidant capacity related to their aromatic character, lignins and wood extracts can quench the unstable-free radicals formed during the degradation of hemicelluloses by reactions of radical transfer to form stable phenoxyl radicals. These species were detected by ESR even if it is impossible by this technique and under our conditions to distinguish the phenoxyl radicals resulting either from lignin or from the extracts. Furthermore, correlation between modifications of wood colour induced by heat treatment and the concentration of these radicals was observed.

References

Ahajji A, El Bakali I, George B, Merlin A (2003) Analyse par spectroscopie de résonance paramagnétique électronique (RPE) de bois traités thermiquement exposés à un rayonnement de type solaire. 6$^{\text{èmes}}$ Journées Scientifiques de la Forêt et du Bois – Epinal. Annales du GIS bois/environnement, pp 175–182

Avat F (1989) Nature et rôle des extractibles dans la rétification du bois. DEA ENSM.SE, Saint Etienne

Avat F (1993) Contribution à l'étude des traitements thermiques du bois (200–300°C): transformation chimique et caractéristiques physico-chimiques. Thèse de doctorat, Ecole des mines de St-Etienne

Bourgois J, Guyonnet R (1988) Characterization and analysis of torrefied wood. Wood Sci Technol 22:143–155

Brand-Williams W, Cuvelier ME, Berset C (1995) Use of a free radical method to evaluate antioxidant activity. Food Sci Technol 28:25–30

Chrisment A (2000) Color by the numbers. CD ROM DATACOLOR International. Editions 3C – Conseil, Paris

Dirckx O, Triboulot MC, Merlin A, Deglise X (1992) Modifications de la couleur du bois d'*Abies grandis* exposé à la lumière solaire. Ann Sci For 49:425–477

Fengel D, Wegener G, Heizmann A, Przyklenk YM (1978) Analyse von Holz und Zellstoff durch Totalhydrolyse mit Trifluoressigsäure. Cell Chem Technol 12:31–37

Fengel D, Uçar H, Wegener G (1979) Isolation and characterization of the polysaccharides from beechwood (*Fagus sylvatica* L.). Papier 33:233–239

Hakkou M, Petrissans M, El Bakali I, Gerardin P, Zoulalian A (2003) Study of the influence of temperature on the wetting of thermal treated wood by light pyrolysis. 9ème Congrès de la SFGP, pp 509–516

Hawkes GE, Smith CL, Utley JHP, Vargas RR, Vierther H (1993) A comparison of solution and solid state ^{13}C NMR spectra of lignin and lignin model compounds. Holzforschung 47:302–312

Ishiguri F, Saitoh K, Andoh M, Abe Z, Yokota S, Yoshizawa N (2000) Improvement of heartwood color of black-colored sugi (*Cryptomeria japonica* D. Don) by UV irradiation after smoke-heating. Holzforschung 54:294–300

Ishiguri F, Maruyama S, Takahashi K, Abe Z, Yokota S, Andoh M, Yoshizawa N (2003) Extractives relating to heartwood color changes in sugi by a combination of smoke-heating and UV radiation exposure. J Wood Sci 49:135–139

Janin G (1987) Mesure de la couleur: intérêt forestier et industriel. Ann For Sci 44:455–472

Kamdem P, Pizzi A, Triboulot MC (2000) Heat treated timber potentially toxic side products presence and wood cell wall degradation. Holz Roh Werkst 58:253–257

Kamdem DP, Pizzi A, Jermannaud A (2002) Durability of heat-treated wood. Holz Roh Werkst 60:1–6

Kilcullen F (1995) Caractérisation du chêne rétifié: extractibles polaires et apolaires, comportement thermique, mouillabilité, couleur. DEA ENSM.SE, Saint Etienne

Kotilainen R (2000) Chemical changes in wood during heating at 150–260 C. Ph.D. thesis, Jyväskylä University. Research report 80, Finland

Mazet JF (1988) Couleur et qualité des placages de chêne et étude de leur comportement photochimique. Thèse de doctorat de l'Université H Poincaré Nancy 1

Mazet JF, Triboulot MC, Janin G, Merlin A, Deglise X (1993) Modifications de la couleur du bois de chênes européens exposé à la lumière solaire. Ann Sci For 50:119–146

Merlin A, Deglise X (2001) Comportement photochimique du bois non traité. In: Durabilité des bois et problèmes couplés. Hermès Sciences, Paris

Mitsui K, Tsuchikawa S (2005) Low atmospheric temperature dependence on photodegradation of wood. J Photochem Photobiol B Biol 81:84–88

Mouras S, Girard P, Roussin P, Permali P, Dirol D, Labat G (2002) Propriétés physiques de bois peu durables soumis à un traitement de pyrolyse ménagée. Ann For Sci 59:317–326

Nuopponen M, Vuorinen T, Jämsä S, Viitaniemi P (2005) Thermal modifications in softwood studied by FT-IR and UV resonance raman spectroscopies. J Wood Chem Technol 24:13–26

Roy C, Pakdel H, Brouillard D (1990) The role of extracts during vacuum pyrolysis of wood. J Appl Polym Sci 41:337–348

Rousset P (2004) Choix et validation expérimentale d'un modèle de pyrolyse pour le bois traité par haute température: de la micro-particule au bois massif. Doctorat en Sciences forestières et du bois, ENGREF

Sandermann W, Augustin H (1964) Chemical investigation on the thermal decomposition of wood: Part III. Holz Roh Werkst 22:377–386

Singleton VL, Rossi JA (1965) Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. Am J Enol Viticult 16:144–158

Sivonen H, Maunu SL, Sundholm F, Jämsa S, Vitaniemi H (2002) Magnetic resonance studies of thermally modified wood. Holzforschung 56:648–654

Tjierdsma B, Boonstra M, Pizzi A, Tekely P, Militz H (1998) Two-steps heat timber: molecular level reasons for wood performance improvement. Holz Roh- Werkst 56:149–153

Triboulot MC (1993) Photostabilisation de la couleur du matériau bois. Thèse de doctorat de l'Université H Poincaré, Nancy 1

Van Acker J, Homan W, Jones D (2004) Wood modification developments. Proceedings – Annual Meeting of the American Wood-Preservers' Association 100, pp 55–59

Varga D, Van der Zee ME (2008) Influence of steaming on selected wood properties of four hardwood species. Holz Roh Werkst 66:11–18